

The University of Chicago

THE ABSORPTION SPECTRA
OF SAMARIUM ION IN THE CRYSTAL LAT-
TICES OF SAMARIUM TUNGSTATE
AND SAMARIUM MOLYBDATE

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1935

By
EDWARD LAUTH HAENISCH

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THE ABSORPTION SPECTRA OF SAMARIUM
ION IN THE CRYSTAL LATTICES OF
SAMARIUM TUNGSTATE AND SAMARIUM MOLYBDATE

Investigations of the absorption spectra of samarium ion in the crystal lattices of hydrated salts and the temperature variation thereof have been published.¹ The lines and bands thus reported are interpreted as arising from the basic multiplet which is produced by the splitting of the degenerate $6H_{5/2}$ level (as predicted by Hund²) by the electric fields of the surrounding ions in the lattice.³ The temperature variations in the intensity and width of the lines and multiplets have been accounted for by the consideration of the three factors: (a) the lattice contraction and expansion, (b) the thermal vibration of the lattice and (c) the Boltzmann distribution. The splitting of the basic multiplet as predicted from a study of the spectrum has been confirmed in the case of samarium sulfate octahydrate ($Sm_2(SO_4)_3 \cdot 8H_2O$) by an investigation of the variation of the magnetic susceptibility with the temperature⁴ and by an examination of the specific heat data.⁵

¹S. Freed and J. G. Harwell, J. Am. Chem. Soc., **55**, 74 (1933).

F. H. Spedding and R. S. Bear, Phys. Rev., **42**, 58, 76 (1932); **44**, 287 (1933); **46**, 308, 975 (1934).

F. Ephraïm and P. Ray, Ber., **62B**, 1639 (1929).

²F. Hund, Z. Physik, **33**, 855 (1926).

³The Stark effect accounts for a splitting of $6H_{5/2}$ into three levels at most. In $Sm_2(SO_4)_3 \cdot 8H_2O$ at least four levels have been predicted. Other coupling effects between the fields of the lattice and of the Sm ion must be considered.

⁴S. Freed, J. Am. Chem. Soc., **52**, 2702 (1930).

⁵J. E. Ahlberg and S. Freed, ibid., **57**, 431 (1935).

The present work was undertaken to observe the changes that might be introduced in cases in which the samarium ion was situated in the lattices of anhydrous crystals. The salts, samarium molybdate ($\text{Sm}_2(\text{MoO}_4)_3$) and samarium tungstate ($\text{Sm}_2(\text{WO}_4)_3$), were chosen because their melting points were within the range of the furnace which was available. The choice of these salts had a further advantage, namely, the possibility of determining the emission spectrum of the samarium ion in the same lattice as its absorption spectrum was to be determined. Many natural minerals which contain tungstates or molybdates are fluorescent because of the presence of small amounts of mixtures of the rare earths. Attempts to prepare synthetic minerals containing only samarium as the fluorescent substance failed because high enough temperatures were not available to melt the base substances, such as calcium tungstate.

Tomaschek and Deutschbein⁶ have attempted to compare the emission and absorption spectra. They were forced to make their comparison between the emission spectrum of samarium ion in calcium sulfide phosphors and the absorption spectrum of samarium ion in the crystal lattice of hydrated samarium sulfate. Such results are not particularly significant since the samarium ion is subjected to entirely different fields and surroundings in the two substances. In general, these investigators have found one or two emission lines which correspond roughly to absorption bands, and in addition, many emission lines farther to the red than any known absorption regions.

⁶R. Tomaschek and O. Deutschbein, Z. Physik, 82, 309 (1933).

EXPERIMENTAL

Preliminary experiments were conducted with samarium phosphate (SmPO_4). This salt, like all others used in this study, was prepared by the addition of a solution of the appropriate sodium salt, here tri-sodium phosphate, to a samarium chloride solution. The phosphate thus obtained did not melt in an oxygen-gas blast flame, but did melt in an oxyhydrogen flame. At this temperature the phosphate glowed brilliantly with a white light. Since this temperature was far above that available in the furnace many attempts were made to prepare the crystalline anhydrous salt by heating a mixture of sodium metaphosphate, sodium chloride and samarium oxide to $900 - 1000^\circ \text{C}$. for ten to twelve hours and then cooling very gradually. No crystals of any appreciable size were obtained when the melt was extracted with water. P. T. Cleve⁷ had reported success with this method.

Similar experiments with the arsenates and the vanadates showed that they also had too high melting points.

The molybdate and the tungstate which were finally used were prepared in the following manner. Every precaution was taken to eliminate all contaminations such as dust particles, lint, filter paper fibers, etc., since these might not only serve as nuclei for the growth of small crystals, but also they might cause the reduction of either molybdate or tungstate.

The samarium oxide which was used in the final preparations was a portion of an extremely pure sample kindly furnished

⁷P. T. Cleve, Chem. News, **53**, 91 (1886).

by Professor B. S. Hopkins of the University of Illinois.

The samarium oxide was dissolved in hydrochloric acid and the excess acid removed by evaporation on the water bath. The samarium chloride was then dissolved in water and the solution filtered through a sintered glass disc to remove particles. The solution was diluted to a large volume and the precipitating agent (sodium molybdate or sodium tungstate) added dropwise and with constant stirring to minimize occlusion. The precipitates were white to very pale yellow in color and very gelatinous. They were separated from the supernatant liquid by centrifuging and washed with water five to eight times by the same method. The final filtrations were carried out through a sintered glass plate.

An enormous shrinkage in volume occurred when these hydrated solids were heated to dull redness. They were, therefore, "pre-shrunk" by heating for several hours at 900° C. before they were put into the large furnace in which the crystal growth was to proceed. During this heating the color changed from pale yellow to a deeper shade. A continuous current of oxygen was passed into the heating chamber to prevent reduction of the precipitate.

The furnace used was a molybdenum-wound resistance type which delivered about 1500° C. at 70 amperes. The inner core was a non-porous Sillimanite cup capable of withstanding high temperatures. This was used to prevent the diffusion of the hydrogen which had to stream around the wire to prevent the oxidation of the molybdenum. The alundum cover was shielded with platinum so that no particles could fall into the melt. A slow counter stream of oxygen was passed into the Sillimanite cup during the fusion to prevent any possible reduction of the tungstate or molybdate. The furnace was mounted in a concrete

pier to reduce vibration to a minimum. The temperature was measured with a platinum, platinum-rhodium thermocouple.

A method of crystal growth developed by S. Kyropoulos⁸ was employed. The melt was heated to about 150° above the fusion point in order to destroy any nuclei around which crystal growth might start. After this temperature had been maintained for one hour a platinum tube, T, (Fig. 1) was inserted into the liquid. The motion of this tube was controlled by a rack and pinion mounted on a firm support. Usually the tube was inserted to a depth of 3 - 5 mm. When the temperature had fallen to 70° above the melting point, a slow current of air was started flowing through the tube and Part A (Fig. 1) began to form. When this globule had reached a diameter of 1 - 2 cm. the tube was slowly withdrawn until merely a thread upon which Part B was to grow was left in contact with the melt. The air blast was strengthened in order to cause B to grow. Conditions were adjusted so that A grew in fifteen to thirty minutes and B, in one to two hours. When B had reached the desired size, the tube was lifted above the residual liquid in the platinum crucible and the air stream was slowly stopped. The electric current was very gradually reduced so that the complete cooling of the fur-

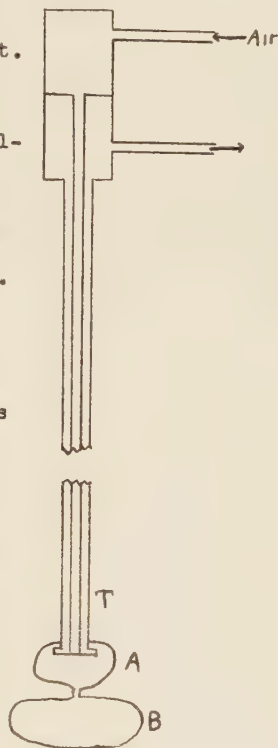


Fig. 1

⁸S. Kyropoulos, Z. Physik, 63, 849 (1930).

nace took more than twenty four hours. At no time were large crystals obtained but fragments about 1 mm. thick and 3 - 5 mm. on a side could be chipped out of the conglomerate of small crystals. Many difficulties were encountered in the proper adjustment of the height of the tube because of the poor visibility.

The absorption spectra of these crystal fragments were photographed with a three glass prism Steinheil spectrograph. (Photographs of crystals of sodium tungstate and molybdate showed that they did not transmit light appreciably below 3700 - 3800 $\text{\AA}$.) The technique used was similar to that previously reported.⁹ The crystals were mounted in cork strips and suspended in a quartz Dewar with plane windows. Baths of liquid nitrogen (78° K.), liquid ethylene (169° K.) and liquid methane (113° K.) were used. All these liquids were filtered through cotton before they entered the Dewar in order to remove any ice particles which might scatter the light. An ordinary projector lamp was used as the source of illumination. The optical system required exposures of five to fifteen minutes with the W & W panchromatic plates which were used.

The wave lengths of the lines and bands of the spectra were determined by comparison with an iron arc spectrum printed on the plates above and below each absorption strip. In the computations the Hartmann interpolation formula was applied over regions of 200 $\text{\AA}$. In each region several iron lines were also measured and these checked the known values within $\pm 0.05 \text{\AA}$, which agreement showed that no error had been made in the identification of the iron spectrum. For the samarium spectra the accuracy of a sharp line is $\pm 0.5 \text{ cm.}^{-1}$ and of the more diffuse

⁹S. Freed and F. H. Spedding, *Phys. Rev.*, 34, 945 (1929).
F. H. Spedding and R. S. Bear, *ibid.*, 42, 58 (1932).

bands, $\pm 5 \text{ cm.}^{-1}$. Some difficulty was encountered in setting upon the centers of these very faint and diffuse bands.

Numerous attempts were made to obtain a "calcium tungstate mineral" which contained only traces of samarium as a fluorescent substance. Calcium tungstate which was prepared by the addition of recrystallized sodium tungstate solution to a calcium chloride solution manufactured by dissolving calcite in hydrochloric acid was fluorescent. The original calcite was non-fluorescent. To complicate the problem further the calcium tungstate did not melt at the highest temperature (1500° C.) furnished by the furnace. It may be noted, however, that when 0.1 per cent of samarium tungstate was added to the calcium salt and the mixture heated at 1400° C. for several hours a very faint red fluorescence was observed when the exciting source was a carbon arc with a Corex filter.

Experiments were tried with lanthanum tungstate as a base but, upon heating, this salt not only did not melt but it showed definite evidence of decomposition into the oxides. This is in accord with the observations of Jander¹⁰ on the changes in crystal structure at high temperature.

Further attempts at fluorescence studies must be delayed until higher temperatures are procured to make crystals of calcium tungstate.

¹⁰W. Jander, Z. anorg. chem., 192, 286, 295 (1930).

RESULTS

P. T. Cleve¹¹ has reported samarium molybdate as violet rhombic octahedra which she obtained by calcining a mixture of samarium oxalate, molybdenum trioxide and sodium chloride. F. Zambonini and R. Levi¹² showed that samarium and the alkaline earth molybdates are isomorphic. G. Carobbi¹³ has assigned samarium molybdate to the tetragonal class with $a:c = 1:1.5745$. He reported the color and appearance as pale yellow tetragonal bipyramids.

The samarium molybdate which was obtained was dark yellow in color; several times small pyramids were chipped out of the crystal conglomerate. The salt started to melt in the furnace about 1050°C . No accurate determination of the melting point was made.

Prints of the spectrum taken at four different temperatures are shown in Fig. 2. A print of the spectrum of samarium chloride hexahydrate at liquid nitrogen temperatures is included for comparison purposes.

The bands were so diffuse that their position has been recorded only for liquid nitrogen temperatures. These positions are given in Table I.

¹¹P. T. Cleve, Chem. News, 53, 93 (1886).

¹²F. Zambonini and R. G. Levi, Atti accad. Lincei, (6) 2, 462 (1925).

¹³G. Carobbi, Rend. accad. sci. fis. mat. Napoli, 31, 83 (1925).



Fig. 2 - Absorption bands of samarium molybdate. 1, 2, 3 and 4 are the absorption spectra of the salt at the temperatures noted at the left. 5 is the absorption spectrum of hydrated samarium chloride at liquid nitrogen temperatures.

TABLE I
ABSORPTION BANDS OF SAMARIUM MOLYBDATE AT 78° K.

Intensity was estimated on a rough scale of 10 with very faint lines considered as 0. S(sharp) and d(diffuse) are used to indicate the character of the edges.

Wave Length	Wave Number	Intensity
5635.8	17,739 }	2d
5624.9	17,773 }	2d
5304.4	18,847 }	3d
5292.5	18,889 }	3d
5019.7	19,916 }	1d
5013.6	19,940 }	1d
5005.5	19,972 }	0d
5000.0	19,994 }	0d
4913.3	20,347 }	8s
4904.8	20,382 }	8s
4822.0	20,733 }	0d
4792.7	20,859 }	0d
4773.1	20,945 }	1d
4765.4	20,979 }	1d
4753.7	21,030 }	0d
4726.9	21,150 }	0d
4656.6	21,469 }	0d
4645.9	21,518 }	0d
4634.2	21,573 }	1d
4622.6	21,627 }	1d
4523.1	22,103	*

TABLE I - CONTINUED

Wave Length	Wave Number	Intensity
4219.5	23,693 }	Od
4161.5	24,023 }	Od
4093.1	24,424	**

*The region around this value is very diffuse.

**Transmission ceases.

The crystal fragments of samarium tungstate were paler yellow than those of samarium molybdate. The tungstate melted about 1150° C. This was not the exact melting point but merely the temperature at which first evidences of fusion could be observed in the furnace. No definite crystal forms were found in the conglomerates.

Prints of absorption spectrum of samarium tungstate at four different temperatures are shown in Fig. 3. A print of the absorption spectrum of hydrated samarium chloride is included for purposes of comparison. For the liquid ethylene (169° K.) and the liquid methane (113° K.) two prints are included. In each case one photograph was printed exceptionally dark (with a resultant blurring of the blue region) to bring out the extremely faint structure of the red region of the spectrum.

The wave lengths of the lines and bands at liquid nitrogen temperature are given in Table II and for liquid methane temperature in Table III.

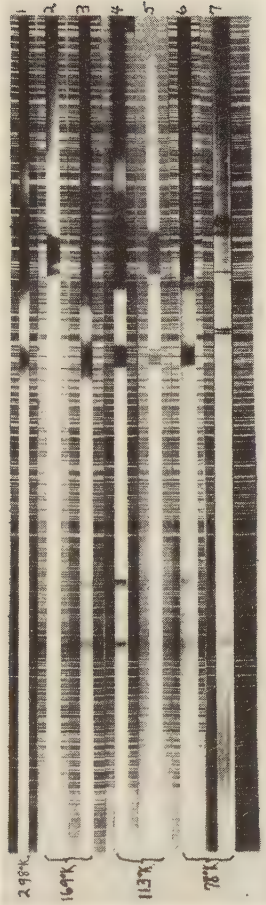


Fig. 3 - Absorption lines and bands of samarium tungstate. 1 to 6 inclusive are spectra of the tungstate at the temperatures marked at the left. 3 and 4 are prints which were overexposed in the blue to bring out the very faint structure in the red region. 7 is the absorption spectrum of hydrated samarium chloride at liquid nitrogen temperatures.

TABLE II

ABSORPTION LINES AND BANDS OF SAMARIUM TUNGSTATE AT 78° K.

Intensity was estimated on a rough scale of 10 with very faint lines considered as 0. S(sharp), d(diffuse), b(broad) and vb(very broad) are used to indicate the character of the lines and edges. Primes values are band edges.

Wave Length	Wave Number	Intensity
5645.6	17,708.0	0s
5636.7	17,736.0	1s
5311.6	18,821.5	1s
5306.3	18,840.3	2s
5020.6	19,912.4	5s
5014.9	19,935.0	1sd
5007.4	19,964.9	1sd
4992.3	20,025.3	0d
4984.9	20,055.0	0d
4920.7	20,316.7	2d
4913.9	20,344.8	3s
4909.8	20,361.8	3s
4899.3	20,405.4	4sd
4891.7	20,437.1	4sd
4885	20,465	0b
4876.5	20,502	0b*
4865.3	20,549.0	0vb
4855.4	20,589.9	0b
4842.2	20,646.0	0b
4829	20,702	} 1b
4821.6	20,734.2	
4814.5	20,764.3	

TABLE II - CONTINUED

Wave Length	Wave Number	Intensity
4806	20,801 }	2b
4782	20,906	1vb*
4774.5	20,938	1vb*
4766	20,976	1vb*
4758.5	21,009	1vb*
4751.4	21,040.6	1vb*
4743.5	21,075.6	1vb*
4736.3	21,107.5' }	2d
4721.2	21,172.2' }	2d
4715.5	21,200	0vb
4657	21,467' }	0d
4652	21,490 }	0vb
4639.6	21,547.5 }	5vb
4630.5	21,590' }	1d
4530.4	22,066.9	5s
4524.9	22,093.8	0s
4520.8	22,113.8	0s
4514.8	22,143.2	3s
4456.1	22,434.9	0b*
4417	22,633	vfvd*
4411.5	22,662	vfvd*
4405	22,690	vfvd*
4401	22,716	vfvd*
4206.5	23,766' }	10sd
4201.8	23,792.6' }	10sd
4200	23,803' }	8sd
4197	23,820' }	5sd

TABLE II - CONTINUED

Wave Length	Wave Number	Intensity
4195.6	23,827.8' }	5sd
4189.5	23,862.5' }	2d
4186.9	23,877.3	3vd
4184	23,894' }	2d
4180.2	23,917' }	10sd
4096.8	24,402.4	4s
4093.0	24,425.1 }	1sd
4091.4	24,434.6 }	6s
4090.1	24,442.4 }	6s
4088.2	24,453.7 }	2d
4083.8	24,480.1	3s
4078.6	24,511.3	2vb
4075.6	24,529.4' }	4d
4072.5	24,548' }	2d
4064	24,599' }	2vd
4027	24,825' }	0vd
4019	24,875	Od ^{**}
3998	25,005	Od
3994	25,031	Od
3991.5	25,045' }	Od
3988	25,068' }	Od
3986	25,081' }	Od
3980	25,118' }	Od
3935	25,406	Od
3931	25,430	Od
3914	25,540	Od
3911	25,559	Od

TABLE II - CONTINUED

Wave Length	Wave Number	Intensity
3907	25,587	Od
3905	25,600	ld
3897	25,648	Od
3799	26,310	***

* May be 2 - 3 A° wide.

** Region from this point to the blue is very faint and difficult to discern.

*** Transmission ceases.

TABLE III

ABSORPTION LINES AND BANDS OF SAMARIUM TUNGSTATE AT 113° K.

Intensity was estimated on a rough scale of 10 with very faint lines considered as 0. (Some rather doubtful lines indicated by 00.) S(sharp), d(diffuse), b(broad), vb(very broad) are used to indicate the character of the lines and edges. Primed values are band edges.

Wave Length	Wave Number	Intensity
5646.3	17,705.8	00s
5637.3	17,734.1	00s
5312.8	18,817.2	00s
5308.1	18,833.9	00s
5020.6	19,912.4	1d
4992.8	20,022.9	00d
4984.1	20,058.2	00d
4921.1	20,315.0	00d
4914.0	20,344.4	3d
4910.2	20,360.1	2d
4899.5	20,404.6	1d
4892.0	20,435.8	1d
4876	20,503	vbvf
4866	20,545	vbvf
4857	20,593	vbvf
4843	20,643	vbvf
4831	20,690'	} } 2d
4827	20,711'	
4823.2	20,726.5'	
4820.4	20,739.4'	
4816.7	20,755.3'	
4811.1	20,779.0'	2d

TABLE III - CONTINUED

Wave Length	Wave Number	Intensity
4805.1	20,805.4	2d
4783.4	20,899.8' }	2s
4779.2	20,918.2' }	2s
4767	20,973	vbvf
4751	21,042	vbvf
4743	21,077	vbvf
4736.0	21,109.0' }	1d
4720.3	21,179.2' }	1d
4715.5	21,201	0vd
4657.2	21,466.1' }	2d
4649.2	21,503.1' }	2d
4645.1	21,522.1	2d
4641.5	21,538.7' }	3d
4636.4	21,562.4' }	5d
4530.5	22,065.9	5s
4524.9	22,093.7	0sd
4520.7	22,114.3	0sd
4514.9	22,142.7	1s
4419	22,623' }	0d
4400	22,720' }	0d
4257.2	23,762.1' }	10s
4201.7	23,793.2' }	8s
4199.9	23,803.4' }	8s
4197.6	23,816.5' }	5s
4196.0	23,825' }	2s
4190.2	23,858.5' }	2d
4187.3	23,875.0	0vd

TABLE III - CONTINUED

Wave Length	Wave Number	Intensity
4184.3	23,892.1' }	2d
4181.0	23,911.0' }	7s
4097.3	24,399.4' }	5d
4095.0	24,413.2' }	5d
4092.9	24,425.7' }	8s
4091.2	24,435.8' }	3d
4090.8	24,438.2' }	2d
4089.6	24,445.4' }	2d
4089	24,450' }	0d
4087.3	24,459.1' }	8s
4084.7	24,475.2' }	5d
4082.2	24,489.7' }	2d
4079.8	24,504.1' }	1d
4077.5	24,518' }	0d
4076.8	24,522' }	0d
4023.5	24,847' }	0d
3998	25,007	vfd

DISCUSSION OF RESULTS

The bands in the spectrum of samarium molybdate were not resolved even at liquid nitrogen temperatures. No changes in relative intensities of the respective bands were observed in the plates taken at the various temperatures. The only effect was that the bands became more diffuse and less definite at the higher temperatures. An explanation for this blurring may be sought in the indefiniteness of the positions and the thermal vibrations of the atoms or ions which surround the samarium ion in the crystal lattice. The changes in temperature may also bring about changes in the transition probabilities. Zambonini and Levi¹⁴ in some preliminary work have reported samarium molybdate as a crystal of the pseudo structure type, a fact which indicates that some samarium ions are surrounded by fields slightly different from others. This observation is in accord with the facts known for a mixed salt of samarium mercury chloride.¹⁵ There still remains the very interesting problem of the changes that arise in the absorption spectra at liquid hydrogen temperatures at which the amplitude of the thermal vibrations in the lattice would be very small.

The position of the bands of samarium molybdate are dis-

¹⁴F. Zambonini and R. G. Levi, op. cit.

¹⁵S. Freed and E. L. Haenisch, unpublished work. The spectrum of the mixed salt at liquid nitrogen temperatures consisted of bands which were similar in appearance to those of samarium molybdate. Professor Zacharisen of the Physics Department very kindly investigated the crystal structure of the mixed salt. He found the unit cell to be complicated and to contain two types of samarium ions, i. e. samarium ions surrounded by two different atomic arrangements.

placed toward the red from the position of the lines of the absorption spectrum of hydrated samarium chloride.

With respect to the chloride as a standard the samarium tungstate spectrum is displaced further to the red than is the spectrum of the molybdate. The multiplets of the tungstate spectrum are wider and more complicated in structure than those of the chloride. The tungstate spectrum contains a very few extremely sharp lines at liquid nitrogen temperatures. Most of the structure, however, is very diffuse and there are many unresolved bands. The remarkable contrast between the tungstate and molybdate spectra points to fundamental differences in the arrangements of the unit cells of these two salts. No data are available for the crystal structure of the tungstate.

In the previous studies of the absorption spectra of the hydrated samarium salts the levels close to the basic level were located by means of the variations with the temperature in the relative intensities of the components of the multiplets with respect to each other. These variations were easily apparent upon a visual examination of the plates. This intensity variation occurred because of the change in the population of the levels close to the basic one as the temperature varied. The population of a level, $\frac{e^{-E}}{kT}$, as regards temperature, depends on the Boltzmann factor, $e^{-\frac{E}{kT}}$, where E is the height of the level in cm.^{-1} above the basic level, k is the Boltzmann constant in the proper units ($0.7 \text{ cm.}^{-1} \text{ deg.}^{-1}$) and T is the absolute temperature.

For the case of the tungstate the spectrum had become so blurred and so faint at liquid ethylene and room temperatures that observation of the intensity changes had to be limited to a study of the plates at liquid nitrogen and liquid methane temperatures. (It was necessary to give very long exposures to obtain

structure at liquid methane temperatures.) Since the Boltzmann factors are not very different for these two temperatures (78° K. and 113° K.) the plates were microphotometered.¹⁶

The curves for the two temperatures showed a definite change in relative intensity only for the multiplet at about $4520 \text{ \AA}^{\circ}$ ($22,100 \text{ cm.}^{-1}$). These curves are shown in Fig. 4.

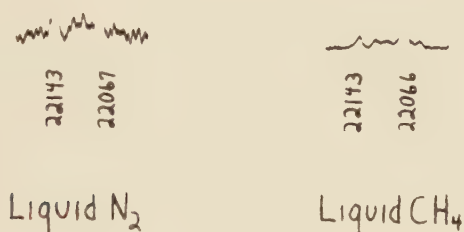


Fig. 4 - Microphotometer curves of the $4520 \text{ \AA}^{\circ}$ multiplet.

This change in intensity was visible to the eye. It was verified on several different plates at both temperatures. The multiplet was just barely visible on a plate taken at liquid ethylene temperatures. At this higher temperature the red component was by far the stronger in intensity.

Thus it appeared that there was a level 76 cm.^{-1} above the basic level in samarium tungstate.¹⁷ This interval has been

¹⁶A Moll microphotometer was used through the courtesy of the Physics Department.

¹⁷A study of the intervals in the spectrum showed that the following intervals were repeated more than five times. These were intervals which were maintained with changes in temperature, *i. e.*, both components were shifted the same amount in the same direction. No intensity variations with the temperature could be observed. The intervals were 30, 35, 40, 50, 60, 75, 90 and 105 cm.^{-1} . Presumably, these are to be attributed to activated states.

noted between band edges in other portions of the spectrum but nothing positive can be concluded from these edges.

The other levels, in case there are more than one, may lie close to the basic one. That it will be necessary to have liquid hydrogen to establish the presence or absence of these levels is evident from the Boltzmann factors give in Table IV. At this temperature the spectrum may become much sharper and more definite.

TABLE IV
BOLTZMANN FACTORS

Interval cm. ⁻¹	Relative Number in Higher Level		
	20° K.	78° K.	113° K.
20	.239	.691	.779
40	.057	.482	.601
60	.014	.333	.468
80	.003	.230	.364
100	.0009	.160	.320

To complete the study of these two salts it will be expedient to study accurately the arrangements of the atoms in the unit cells and to study the spectra at liquid hydrogen temperatures.

This thesis presents a portion of the data which must be gathered before the chemistry and physics of the solid state can be understood and theories of behavior of the solid state established.

SUMMARY

1. Anhydrous crystals of samarium molybdate and samarium tungstate were prepared.

2. Their absorption spectra were investigated at various temperatures and found to consist chiefly of diffuse structure. Some sharp lines were observed in the samarium tungstate spectrum at 78° K. and at 113° K.

3. A difference between the crystal structures of the molybdate and the tungstate was postulated because of marked differences in the structures of the spectra of the two substances.

4. A level at 76 cm.^{-1} above the basic level was tentatively assigned to samarium tungstate. Further investigation will require the use of liquid hydrogen.

